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S/190/60/002/02/11/011
B004/B061

5.3831

AUTHORS: Spirin, Yu. L., Gantmakher, A. R., Medvedev, S. S.
TITLE: Electron Absorption Spectra of Carbanions in the
Polymerization of Styrene in the Presence of Organometallic
Compounds
PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 2,
pp. 310-312

TEXT: The authors proceed from the data published in Refs. 1-4,
according to which the composition of copolymers changes when, instead
of organosodium, organolithium compounds are used as catalysts, and the
polymerization occurs in hydrocarbons instead of in amines and ethers.
The polymerization is accelerated by the conversion of LiR to NaR and
the substitution of amines, ether, or tetrahydrofuran for hydrocarbon.
The authors infer from this that the structure of the carbanion
components of the catalysts for LiR and NaR differ not only in hydro-
carbons but also in polar solvents. This was checked by examining the

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Electron Absorption Spectra of Carbanions
in the Polymerization of Styrene in the
Presence of Organometallic Compounds

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absorption spectra in the near ultraviolet range. The spectra of carbanions formed by polymerization of styrene in the presence of LiR or NaR in different media were taken with an Φ -4 (SF-4) spectrophotometer according to I. V. Astaf'yev's method (Ref. 6), excluding dampness and oxygen. Fig. 1 shows the dependence of the optical density on the wavelength for lithium polystyrene in different media, Fig. 2, the same for sodium polystyrene, and Table 1 gives the absorption maxima. The results are: The absorption maximum is shifted to longer waves (from 330 m μ to 395 m μ) by the use of organosodium compounds. This confirms the strengthening of the carbanion character in NaR as opposed to LiR. The solvent (toluene, toluene + triethylamine, toluene + tetrahydrofuran) has no effect on the position of the absorption bands, and only changes the intensity of absorption. There are 2 figures, 1 table, and 6 references: 3 Soviet and 3 US. X

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

Card 2/g

S/190/60/002/007/012/017
B020/B052

11.2211

AUTHORS: Spirin, Yu. L., Polyakov, D. K., Gantmakher, A. R.,
Medvedev, S. S.

TITLE: Polymerization and Copolymerization of Isoprene Initiated by
Ethyl Lithium .

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 7,
pp. 1082-1092

TEXT: In a previous paper it has been shown (Ref. 1) that the polymeri-
zation mechanism of styrene in the presence of ethyl lithium changes con-
siderably with the transition from a hydrocarbon solvent to a triethyl-
amine toluene mixture. Here, the polymerization and copolymerization laws
of isoprene and styrene by ethyl lithium are investigated under various
conditions. Ethyl lithium was synthesized by reaction of metallic lithium
and ethyl chloride in benzene (Ref. 2). After recrystallization it was
solved in toluene, vacuum-filtered and filled into ampoules. From them,
the solution was filled into the device shown in Fig. 1. The polymeri-
zation was carried out in the dilatometer shown in Fig. 2. The polymers

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were precipitated from the obtained solutions by methanol. During the isolation of polyisoprene, the antioxidant $\text{HCO}_3\text{OH}-\text{A}$ (Neozone-~~B~~) was added to methanol. The polymers were vacuum-dried, and the viscosity of polystyrene in benzene (Ref. 1), and that of polyisoprene in toluene were determined at 30° . The composition of the copolymers was IR-spectrographically and refractometrically determined from their hydrogen and carbon contents on the basis of the supposition that the intrinsic viscosity is an additive quantity. The difference in the results obtained by various methods, was not more than $\pm 2.5\%$. The dependence of the polymerization rate of isoprene on the concentration of the monomer in toluene, ethyl lithium in toluene, triethylamine and the catalyst in a toluene - triethylamine mixture, is graphically presented in Fig. 3. It shows that the polymerization rate is proportional to the monomer concentration. In the toluene - amine mixture, the polymerization rate is proportional to the concentration of the catalyst. However, the dependence of the polymerization rate in hydrocarbons in connection with the lithium polyisoprene association, on the concentration of the catalyst, is more complicated. Fig. 4 shows the kinetic curves of the isoprene and styrene polymerization with 0.003 mole/l of ethyl lithium solution in toluene, and in a toluene -

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amine mixture. The temperature dependence of the polymerization rate of isoprene in toluene and a toluene - amine mixture, is shown in Figs. 5 and 6. Table 1 gives the activation energies and rate constants during the increase of the chains in the isoprene and styrene polymerizations. For comparison, the same quantities are given as to radical polymerization. $E = 14.3$ kcal/mole, $k_{300} = 0.5$ in the polymerization of isoprene in toluene, and in the amine - toluene mixture: $E = 9.2$ kcal/mole, and $k_{300} = 0.03$.

The dependence of $\log [\eta]$ on $\log M$ for polyisoprene in toluene, and toluene with a triethylamine addition, are shown in Fig. 7. Table 2 gives the composition of isoprene styrene copolymers in various solvents at 27°C ; the kinetic curves of the system under different conditions are given in Fig. 8. The constants of the copolymerization of isoprene and styrene in toluene were found to be $r_1 = 9.5$, $r_2 = 0.25$; in a toluene - amine

mixture $r_1 = 1$, $r_2 = 0.8$. On the basis of the results obtained, a polymerization mechanism was suggested for vinyl and diene-monomers in the presence of ethyl lithium under various conditions. There are 8 figures, 2 tables, and 11 references: 6 Soviet and 5 US.

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Polymerization and Copolymerization of Isoprene S/190/60/002/007/012/017
Initiated by Ethyl Lithium B020/B052

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova
(Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: March 17, 1960

Card 4/4

S/190/60/002/008/009/017
B004/B054

AUTHORS: Zabolotskaya, Ye. V., Gantmakher, A. R., Medvedev, S. S.

TITLE: Polymerization of Styrene Under the Action of Complex Catalysts

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 8, pp. 1213-1220

TEXT: The authors attempted to determine the mechanism of polymerization of styrene by combined catalysts of $TiCl_3$ and triisobutyl- or triethyl aluminum. Dosing of aluminum alkyl and $TiCl_3$ was conducted in vacuo by means of the glass vessel shown in Fig. 1. Polymerization was performed in the apparatus of Fig. 2. Vessel 1 contained a ball with aluminum alkyl. The apparatus was evacuated to 10^{-3} mm Hg for 18 hours. In a nitrogen flow, $TiCl_3$ was then filled into the dilatometer 2, and the styrene dissolved in benzene was filled into vessel 3. The content of 3 was poured into 1, the ball with the aluminum alkyl broken, and the whole filled into the dilatometer 2. The dilatometer was melted off the vacuum apparatus at 250-300 mm Hg, ✓

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and polymerization was performed in a thermostat at 75°C . The following results were obtained: 1) There is a proportionality between the polymerization rate w (moles/l·min) and the TiCl_3 concentration: for 0.0228

moles/l of TiCl_3 , $w \cdot 10^2 = 0.186$; for 0.1430 moles/l of TiCl_3 ,

$w \cdot 10^2 = 0.635$. 2) w is a linear function of styrene concentration:

for 0.650 moles/l of styrene, $w \cdot 10^2 = 0.060$; for 3.74 moles/l of styrene, /

$w \cdot 10^2 = 0.379$. 3) The aluminum alkyl concentration (between 0.01 and 0.06 moles/l) and the ratio between TiCl_3 and aluminum alkyl do not affect the

polymerization rate. 4) A study of the temperature dependence of the polymerization rate showed: at 84°C , $w \cdot 10^2 = 0.281$; at 63.5°C , $w \cdot 10^2 = 0.083$.

5) When calculating $w' = w \cdot 10^3 / [\text{TiCl}_3] [\text{styrene}]$, $\log w'$ is a linear function

of $1/T$. The activation energy was found to be 11.0 kcal/mole. 6) 60-70% of the polymer obtained had a molecular weight of 1,000,000 - 1,500,000. The molecular weight did not depend on the monomer concentration. These data indicate a mechanism of polymerization similar to the polymerization of ethylene and propylene: $\text{M}_n^* + \text{M} \rightarrow \text{M}_n + \text{M}^*$. The authors thank Z. V. Zvonkova

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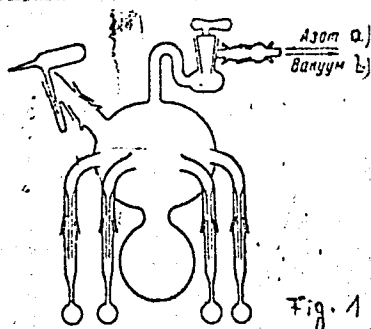
Polymerization of Styrene Under the Action
of Complex Catalysts

S/190/60/002/008/003/017
2004/3054

and N. S. Ivanova for determining the modification of $\alpha\text{-TiCl}_3$, and N. V. Makletsova for determining the molecular weight of the polymers. There are 8 figures, 6 tables, and 15 references: 2 Soviet, 6 US, 1 French, 3 German, and 3 Italian.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova
(Physicochemical Institute imeni L. Ya. Karpov)

SUBMITTED: March 28. 1960



Legend to Fig. 1: Vessel
for dosing the aluminum
alkyl a) nitrogen,
b) vacuum.

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S/190/60/002/009/012/019
B004/B060

AUTHORS: Lanovskaya, L. M., Gantmakher, A. R., Medvedev, S. S.

TITLE: Polymerization of Ethylene by Means of the Combined
Catalyst $\alpha\text{-TiCl}_3$ - AlR_3 in the Presence of Various Monomers.
1 I. The Effect of Various Monomers on the Polymerization of
Ethylene //

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 9,
pp. 1391-1397

TEXT: The authors wanted to study the interaction of various unsaturated compounds with the combined catalyst, and its effect on the polymerization of ethylene under conditions at which these compounds still polymerize at a negligibly low rate. The authors describe the purification of the reagents, the reaction vessel (Fig. 2) with magnetic stirrer and

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Combined Catalyst $\alpha\text{-TiCl}_3$ - AlR_3 in the
Presence of Various Monomers. I. The Effect
of Various Monomers on the Polymerization
of Ethylene

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thermostat, and a device (Fig. 1) which served for introducing the octane solvent and the $(i\text{-C}_4\text{H}_9)_3\text{Al}$ into the reaction vessel. The measurements were made at a constant ethylene pressure of 200 torr by the method developed by A. I. Gel'bshteyn and M. I. Temkin (Ref. 8). The experimental procedure was worked out by Gritsenko and Lanovskaya. α -methyl styrene, isoprene, butadiene, and isobutylene were used as admixtures. In the first series of experiments (Table 1, Fig. 3), the monomer was filled into the reaction vessel before introducing the ethylene. In the second series of experiments (Tables 1, 2, Figs. 4-6), the ethylene was first polymerized during two hours, the monomer was then added, and polymerization was carried on for five more hours. In the experiments specified in Table 1, the authors used TiCl_3 which was obtained from TiCl_4 by reduction by means of antimony. Table 2 specifies

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Combined Catalyst $\alpha\text{-TiCl}_3$ - AlR_3 in the
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the experiments in which TiCl_3 was produced by the reduction of TiCl_4 by means of titanium metal. Experiments revealed that the polymerization rate of ethylene is retarded in the presence of one of the monomer compounds mentioned. The molecular weight of the resulting polyethylene is, however, not influenced thereby. As to their reaction-retarding effect, the various monomer compounds are mentioned in the order butadiene, isoprene > styrene > isobutylene > α -methyl styrene. Diene hydrocarbons, thus, have the greatest retarding effect. The addition of monomers prior to or after the beginning of polymerization bears no influence on this effect. The authors mention a discussion by A. R. Gantmakher on a lecture by A. A. Korotkov at the International Symposium in Prague, 1957. There are 6 figures, 2 tables, and 8 references: 2 Soviet, 4 US, and 2 German. ✓

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Polymerization of Ethylene by Means of the
Combined Catalyst $\alpha\text{-TiCl}_3$ - AlR_3 in the

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B004/B060

Presence of Various Monomers, I. The Effect
of Various Monomers on the Polymerization
of Ethylene

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova
(Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: April 11, 1960

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85424

S/190/60/002/011/010/027
B004/B060

15.8101

AUTHORS: Lanovskaya, L. M., Gantmakher, A. R., Medvedev, S. S.

TITLE: Polymerization of Ethylene by Means of Combined $\alpha\text{-TiCl}_3\text{-AlR}_3$ Catalyst in the Presence of Various Monomers. II. Some Problems Concerning the Polymerization Mechanism in the Presence of Combined Catalysts

PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 11, pp. 1655 - 1658

TEXT: This is a discussion of the results obtained by the authors in Ref. 1 concerning the effect of various monomers on the polymerization of ethylene by $\alpha\text{-TiCl}_3\text{-AlR}_3$ catalysts. The authors' experiments revealed that additions of isobutylene, styrene, isoprene, or butadiene reduce the polymerization rate of ethylene, complexes of these monomers being formed on the catalyst surface. The ability to form complexes is reduced in the series butadiene > isoprene > styrene > isobutylene > α -methyl styrene. This succession is analogous to the series obtained by other researchers for

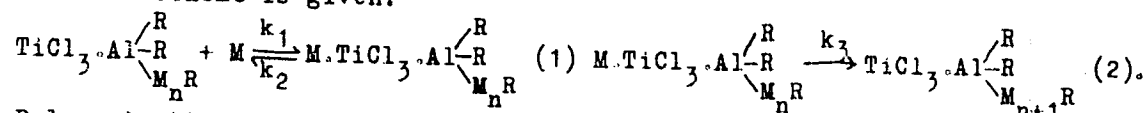
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85414

Polymerization of Ethylene by Means of Combined $\alpha\text{-TiCl}_3\text{-AlR}_3$ Catalyst in the Presence of Various Monomers. II. Some Problems Concerning the Polymerization Mechanism in the Presence of Combined Catalysts

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compounds of platinum, silver, and other metals. The authors base on their experimental results to conclude that the monomers react with the titanium component of the catalyst. A reaction with the aluminum component, which is a Lewis acid, would yield another series of activities. The following reaction scheme is given:



Polymerization by combined catalysts thus does not have a typical anionic course, but is a more complicated process. This has some resemblance with polymerization in the presence of lithium alkyls, but differs from it by specific properties which depend on the structure of the combined catalyst. The authors mention A. A. Babushkin, L. A. Gribov, and A. D. Gel'man. There are 14 references: 5 Soviet, 4 US, 3 British, 1 French, and 1 German.

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85414

Polymerization of Ethylene by Means of Combined $\alpha\text{-TiCl}_3\text{-AlR}_3$ Catalyst in the Presence of Various Monomers. II. Some Problems Concerning the Polymerization Mechanism in the Presence of Combined Catalysts

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B004/B060

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: May 5, 1960

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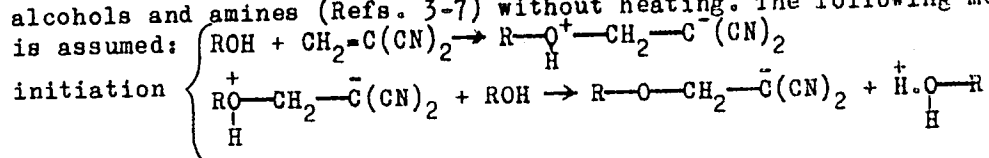
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S/074/60/029/05/02/005
B008/B006

AUTHORS: Gantmakher, A. R., Spirin, Yu. L.
TITLE: Anionic Polymerization Under the Influence of Alkali Metals and Their Derivatives

PERIODICAL: Uspekhi khimii, 1960, Vol. 29, No. 5, pp. 629-647

TEXT: This survey deals with polymerization under the influence of alkali metals and their derivatives. Anionic polymerization proceeds according to an ionic mechanism of the type of an acid-base interaction (Ref. 1), in which the catalysts, or the active centers act as electron donors, while the monomers act as electron acceptors. Vinylidene cyanide and nitro-ethylene monomers, which readily react in anionic polymerization reactions, polymerize in presence of water, alcohols and amines (Refs. 3-7) without heating. The following mechanism is assumed:

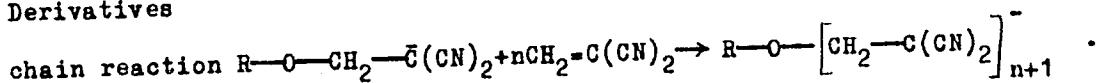


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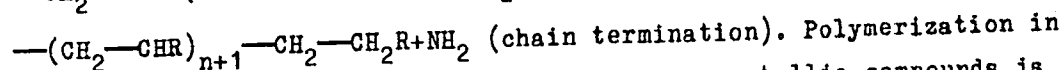
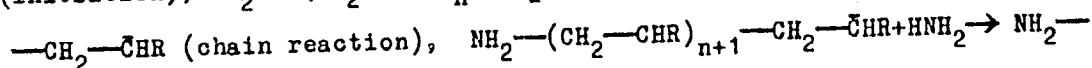
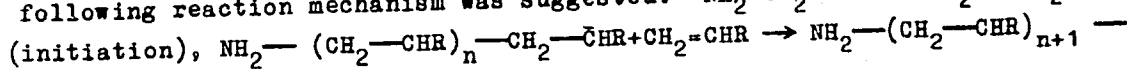
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Anionic Polymerization Under the
Influence of Alkali Metals and Their
Derivatives

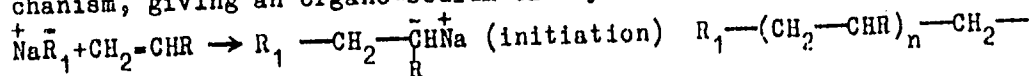
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B008/B006



Refs. 8-13 are the first papers published in the field of polymerization in the presence of alkali metals, amides and organic alkali-metal compounds. Further investigations in this field rendered it possible to clarify the nature of this process. Polymerization in liquid ammonia in the presence of alkali-metal amides is discussed in Refs. 14-16. The following reaction mechanism was suggested: $\bar{NH}_2 + CH_2=CHR \rightarrow NH_2-CH_2-\bar{C}HR$



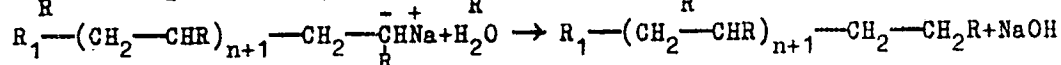
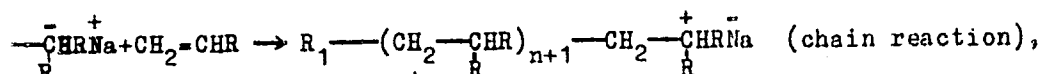
the presence of alkali metals and their organo-metallic compounds is discussed in Refs. 17-35. For this type of reaction, the following mechanism, giving an organo-sodium catalyst as an example, is assumed:



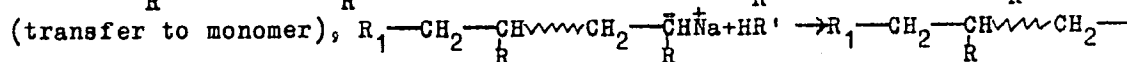
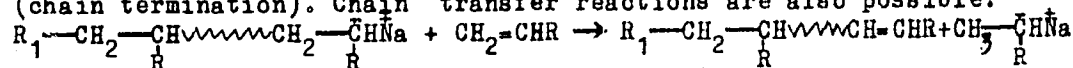
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Anionic Polymerization Under the
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(chain termination). Chain transfer reactions are also possible:



$\text{---CH}_2\text{R} + \text{NaR}'$ (transfer to solvent). It is evident from this reaction scheme that the structure of the growing active center differs little from that of the initial organo-metallic compound. Only the structure of the organic radical bound to the metal changes. The initiation rate depends on the nature of the radical of the initial organo-metallic compound. It can be smaller, equal, or greater than the rate of the chain reaction. It is a special property of organo-metallic catalyst initiated polymerization that, under certain conditions, lengthening of the chain can be continued until the monomer present in the reaction

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mixture is completely used up. The kinetics of polymerization in the presence of alkali metals have scarcely been investigated. Polymerization by metallic lithium and its organic compounds is treated in Refs. 26, 28, 36-55. A special property of monomer polymerization under the influence of organic alkali-metal compounds is that the structure of the polymer chain, and thus also the properties of the polymer formed, depend on the nature of the catalyst and the medium applied (Tables 1, 2). Polymerization in the presence of "alfin" catalysts is described in Refs. 37, 56-62 (the term "alfin" was formed at an early investigation stage of this new catalyst, when it was assumed that only two components - sodium alcoholates and olefine compounds of sodium - were required for its preparation). The mechanism of polymerizations initiated by this catalyst is not yet wholly understood. The nature of the catalyst, however, and rules observed in the reaction, indicate it to be an anionic polymerization. The simultaneous occurrence of anionic- and radical polymerizations in the presence of alkali metals is described in Refs. 23, 63-70. It was shown that the formation of an ion-radical in the reaction of an alkali metal with an unsaturated molecule does not always lead to anionic polymerization. In some cases the competitive radical

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polymerization predominates, while in other cases, both reactions occur simultaneously (Table 3). The preparation of polymers of regular structure - so-called isotactic and syndiotactic polymers - by anionic polymerization methods are described in Refs. 59, 60, 71-80. It is mentioned that stereoregular polymers can be prepared not only in heterogeneous systems, but also in homogeneous mediums, but only in the presence of organo-lithium compounds. Anionic copolymerization is discussed in Refs. 23, 28, 50, 68, 81-90. The latter reaction is widely applied for preparing polymers with valuable properties (Tables 4, 5). It is finally stressed that there is very little quantitative information on the mechanisms of the reactions mentioned in this paper. The following persons are mentioned: I. L. Kondakov, S. V. Lebedev, I. I. Ostromyslenskiy, S. S. Medvedev, A. D. Abkin, O. D. Mamontova, A. A. Korotkov, K. B. Piotrovskiy, V. A. Kropachev, B. A. Dolgoplosk, N. N. Nikolayev, N. N. Chesnokova, L. B. Trukhmanova, G. Mark, Ye. B. Lyudvig. There are 5 tables and 90 references, 22 of which are Soviet.

ASSOCIATION: Fiziko-khimicheskiy in-t im. L. Ya. Karpova
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Card 5/5

GANTHARIE A. R.

To be submitted for the International Symposium on Macromolecular Chemistry,
Montreal, Canada, 27 Jul - 1 Aug 1961.

INDEX

- BOGACHEV, T. M.**, Institute of High Molecular Chemistry, Academy of Sciences USSR, Leningrad, jointly with **BOGACHEV, M. R.**, and **KARPOV, M.**, Dnieper University, Dnepropetrovsk, U.S.S.R. - "Elasticity of cable lattice chain structure" (Group 2)
- BOGACHEV, Boris A.**, and **KARPOV, M. R.**, Dnepropetrovsk, U.S.S.R. - "Interaction of polyethylene with sulphur" (Group 4-5)
- KARPOV, Vladimir A.**, Head, Laboratory of Colloidal Chemistry, Scientific Research Physico-Chemical Institute, Leningrad, U.S.S.R. - "The formation of big crystal structures in polymers" (Group 2, invited lecture)
- BOGACHEV, Boris A.**, and **KARPOV, M. R.**, Dnepropetrovsk, U.S.S.R. - "Polymerization of some epoxy compounds" (Group 3-8) (No. 1)
- BOGACHEV, Boris A.**, **KARPOV, M. R.**, **BOGACHEV, T. M.**, **BOGACHEV, M. R.**, and **KARPOV, M. R.**, Scientific Research Physico-Chemical Institute, Leningrad, U.S.S.R. - "Polymerization catalyzed by lithium and lithium alky" (In German) (Group 3-8)
- BOGACHEV, Boris A.**, **KARPOV, M. R.**, and **BOGACHEV, T. M.**, Scientific Research Physico-Chemical Institute, Leningrad, U.S.S.R. - "On the catalytic polymerization of some epoxy compounds" (Group 3-8)
- BOGACHEV, Boris A.**, **KARPOV, M. R.**, and **BOGACHEV, T. M.**, Scientific Research Physico-Chemical Institute, Leningrad, U.S.S.R. - "Temperature effect on polymer structure in dense polymerization by small crystals" (Group 3-8)
- BOGACHEV, Boris A.**, **KARPOV, M. R.**, and **BOGACHEV, T. M.**, Scientific Research Physico-Chemical Institute, Leningrad, U.S.S.R. - "Study of branching in regular isoprene polymers" (Group 1)
- BOGACHEV, Boris A.**, **KARPOV, M. R.**, and **BOGACHEV, T. M.**, Scientific Research Physico-Chemical Institute, Leningrad, U.S.S.R. - "Nature of molecular-weight distribution and properties of styrene-butadiene rubbers depending on polymerization conditions" (Group 3-4)
- BOGACHEV, Boris A.**, **KARPOV, M. R.**, and **BOGACHEV, T. M.**, Scientific Research Physico-Chemical Institute, Leningrad, U.S.S.R. - "Investigation of the mechanism of polymerization of some epoxy compounds" (Group 3-8)
- BOGACHEV, Boris A.**, **KARPOV, M. R.**, and **BOGACHEV, T. M.**, Scientific Research Physico-Chemical Institute, Leningrad, U.S.S.R. - "Stereoregularity and optical anisotropy of macromolecules" (Group not specified)
- BOGACHEV, Boris A.**, **KARPOV, M. R.**, and **BOGACHEV, T. M.**, Scientific Research Physico-Chemical Institute, Leningrad, U.S.S.R. - "Investigation of the cotton cellulose polydispersity according to the molecular weight" (Group not specified)
- BOGACHEV, Boris A.**, **KARPOV, M. R.**, and **BOGACHEV, T. M.**, Scientific Research Physico-Chemical Institute, Leningrad, U.S.S.R. - "On the mechanism of polymerization of some epoxy compounds" (Group 3-8)

89593

S/190/61/003/002/011/012
B101/B215

15.8/15

AUTHORS: Gantmakher, A. R., Medvedev, S. S., Abkin, A. D.

TITLE: Low-temperature polymerization of ethylene tetrafluoride in liquid phase by the action of gamma radiation

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 2, 1961, 320

TEXT: In this letter to the editor the authors state that they were the first to examine the liquid phase polymerization of ethylene tetrafluoride under the action of gamma radiation. The polymerization was conducted in sealed glass phials in the absence of oxygen, at -55°C and 10 roentgen/sec. Under these conditions, the reaction took place at a high rate and was accompanied by the formation of a solid polymer. After one hour, the yield of polyethylene tetrafluoride was 35%. It was increased up to 95% by a radiation of 6 hr. The studies were continued by Ye. F. Volkova, A. V. Fokin, V. M. Belikov (Tezisy dokladov na II Vsesoyuznom soveshchanii po radiatsionnoy khimii, 1960 str. 65 (Theses of the Reports on the 2nd All-Union Conference of Radiation Chemistry, Moscow, 1960, p. 65) Ref. 1). The

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89593

Low-temperature polymerization of

S/190/61/003/002/011/012
B101/B215

publications show (S. S. Medvedev, A. D. Abkin, P. M. Khomikovskiy, G. N. Gerasimov, V. F. Gromov et al., Vysokomolek. soyed. 2, 904, 1960, Ref. 2) that ethylene under similar conditions is polymerized more slowly. This difference in the polymerization rates of ethylene tetrafluoride and ethylene may be due to a slower rupture of chains by recombination in the polymerization of ethylene tetrafluoride due to repulsive forces. The latter occur in the approximation of perfluorinated radicals of polyethylene tetrafluoride. The slow rate of chain ruptures may also be due to topochemical peculiarities occurring in the polymerization of ethylene tetrafluoride. [Abstracter's note: this is a full translation from the original.] There are 2 Soviet-bloc references.

SUBMITTED: October 29, 1960

Card 2/2

25263

S/190/61/003/007/007/021
B101/B208

15-8610

AUTHORS: Arest-Yakubovich, A. A., Gantmakher, A. R., Medvedev, S.S.

TITLE: Conditions of the formation of metalaromatic initiators of polymerization

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3. no. 7, 1961, 1003-1009

TEXT: The paper deals with the problem of catalytic polymerization, initiated by electron transfer from the atom of the alkali metal to the molecule of an aromatic compound which has a sufficiently high affinity to the electron: $Me + Ar \rightleftharpoons Me^+ + Ar^-$ (1). The general conditions were studied for the course of this reaction, in order to synthesize metal-aromatic complexes of different structure and to study the polymerization mechanism in the presence of such initiators. All operations were performed either in high-vacuum or anhydrous and oxygen-free nitrogen atmosphere. The following results are given: 1) Interaction between alkali metals and aromatic compounds in hydrocarbon medium. To prevent inactivation of the metal by a film from the reaction products with the

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aromatic compound, the experiments were carried out above the melting point of the metal. Sodium gave at 110-120°C in octane or toluene no reaction products with naphthalene or phenanthrene, even after 5-8 hr. With anthracene, Na gave at this temperature a red-violet, at 140-160°C a black powder. This product was completely soluble in tetrahydrofuran (THF) and triethylamine (TEA). These solutions had a characteristic color. The eutectic alloy of K with Na (85% K) quickly reacted with naphthalene and diphenyl at room temperature in hydrocarbon medium. Gray-black powders were formed. No reaction took place in the presence of benzene. In general, however, metalaromatic complexes will also be formed in non-electron-donor medium, if the metal has a low ionization potential and the hydrocarbon a high affinity to the electron. 2) Reactions in TEA medium. Lithium forms with naphthalene a cherry-red solution at room temperature. No reaction was observable with diphenyl even after 10 days. Na with phenanthrene gives only weakly colored solutions, but, with anthracene, quickly a solution which was green in the reflected light, and red in the transmitted light. A greenish-black film is formed on K under the action of naphthalene, which was insoluble in TEA. 3) The metalaromatic complexes were isolated after reaction in THF medium by filtering and subsequent

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evaporation of the solvent in the high vacuum. Sodium-naphthalene decomposed after removing THF to give its initial components, sodium-anthracene was stable. In the complex of potassium-naphthalene, a black powder, the K/naphthalene ratio was 1:1. In the case of lithium-naphthalene, THF could not be completely removed. This is explained by the property of Li to form complexes with ethereal (oxygen-containing) solvents. 4) The initiating effect of metalaromatic compounds was studied on polystyrene. In the presence of Na-naphthalene, polymerization proceeded very quickly not only in pure THF, but also in toluene + 2-4% THF. In the presence of Na-anthracene (about 10^{-3} mole/l) polymerization in toluene + TEA = 1:1 proceeded slowly at 25°C, but was accelerated by a temperature rise. Na-anthracene initiates styrene polymerization also in inert medium (toluene). The solid sodium-aromatic complex dissolves, and the reaction rate increases more and more. 5) To estimate the probability of an interaction between alkali metal and aromatic compound forming soluble products, the following equation is discussed:
 $\Delta E = -L - I + A + S_c + S_a + Q$ (4), where ΔE denotes the change in energy in the reaction, L the sublimation heat of the metal, I its ionization

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potential, A the affinity of the aromatic compound to the electron, S_c , S_a the solvation energy of the cation and anion, respectively, and Q the energy of the coulomb interaction between the latter two. Basing on published data the following is written for the formation rate of metal-aromatic complexes: $Li < Na < K$; benzene $<$ diphenyl $<$ naphthalene $<$ phenanthrene $<$ anthracene. But in some cases the cation of lithium reacts more intensely than K and Na , owing to solvation. A figure illustrates schematically the conditions for the formation of metalaromatic complexes. There are 1 figure, 2 tables, and 29 references: 9 Soviet-bloc and 18 non-Soviet-bloc. The 4 most important references to English-language publications read as follows: M. Szwarc, M. Levy, R. Milkovich, J. Amer. Chem. Soc., 78, 2656, 1956; D.H. Richards, M. Szwarc, Trans. Faraday Soc., 55, 1644, 1959; J.P.V. Gracey, A.R. Ubbelohde, J. Chem. Soc., 1955, 4089; R.M. Hedges, F.A. Matsen, J. Chem. Phys., 28, 950, 1958.

ASSOCIATION: Fiziko-khimicheskiy institut im. L.Ya. Karpova
(Physicochemical Institute imeni L. Ya. Karpov)

SUBMITTED: September 8, 1960

Card 4/5

11.2211 also 2209, 1372

25859
S/020/61/139/004/019/025
B103/B206

AUTHORS: Spirin, Yu. L., Polyakov, D. K., Gantmakher, A. R., and Medvedev, S. S., Academician

TITLE: Polymerization of styrene, butadiene and isoprene, initiated by lithium ethyl in various media

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 139, no. 4, 1961, 899-902

TEXT: The authors investigated the separate polymerization and copolymerization of monomers: a) styrene, b) butadiene, and c) isoprene, which was initiated with lithium ethyl and carried out in 1) toluene, 2) triethylamine (amine), 3) diethyl ether, 4) dioxane, and 5) tetrahydrofuran (THF). Thus, the dependence of the reactivity of these monomers on their structure and on polymerization conditions was to be clarified. The methods were described in previous studies (Ref. 1: Yu. L. Spirin et al., Vysokomolek. soyed., 2, 1082 (1960); Ref. 2: L. M. Lanovskaya et al., ibid., 1391). In all three cases, the molecular weight of the polymers increased in 1)-5) with the intensity of polymerization. Its dependence on the concentration C of the components was close to the ratio M/C (Ref.

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Polymerization of styrene, butadiene ...

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3; M. Szwarc & al. J. Am. Chem. Soc., 78, 2656 (1956), Ref. 4; F. Welch, *ibid.* 81, 1345 (1959)). The walls of the dilatometer were subjected to special treatment when the investigation took place at a low concentration of the initiator ($\sim 10^{-5}$ mole/l). In these cases the concentration of the active centers was determined on the basis of the molecular weight. In the presence of 2) to 5), a bulb dilatometer melted from one piece of quartz was used for polymerization, the concentration of active centers being determined spectrophotometrically at a given wavelength. 1): Even at relatively low concentrations of the initiator, deviations from the proportional dependence of the rate on the concentration of the initiator occurred. The rules observed were previously explained (Ref. 1) by the formation of mutually associated "live" polymers in hydrocarbon media. They are inactive during polymerization. The association of the active centers was also proved viscosimetrically: The viscosity of the solutions of the "live" Li polyisoprene in toluene dropped considerably due to deactivation. The equilibrium between the associates and the monomer centers which are active during polymerization, is displaced with the temperature rise in the direction of the latter. Thus, the activation energy of the process is lowered. This takes place even at a

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Polymerization of styrene, butadiene ...

concentration of the initiator of $\sim 0.5 \cdot 10^{-4}$ mole/l. Thus, an association exists also under these conditions. The authors established that the association of the active centers increases as follows: Li polystyrene < Li polyisoprene < Li polybutadiene. The relative reactivity of the monomers increases as follows: styrene < isoprene < butadiene. 2) - 5): Polymerization is accelerated with the introduction of these solvents, but the activation energies are reduced correspondingly. THF (0.6%) which reduces the activation energy of styrene polymerization in toluene from 14.5 to 6.8, has the strongest effect. However, the activation energy of isoprene polymerization in THF rises with temperature increase. This seems to be explained by a degenerate passing on of the chain through the monomer (Ref. 6: S. Ye. Bresler et al., ZhTF, ser. B, 28, 114 (1958)). The association of the "live" polymers is considerably reduced in the presence of 2) to 5), since 2) to 5) form complexes with lithium. Association of the Li polystyrene is absent in the medium of 2) to 5) (there is a proportional dependence between the rate of polymerization and the concentration of the initiator); Li polyisoprene is slightly associated in amine; Li polybutadiene is considerably associated in

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amine. Even in THF, which is a solvent of high dissolving capacity, some associations of Li polybutadiene occur. This the authors believe to be a dependence of the degree of association of the active centers on their construction. In previous studies (Ref.1; Ref. 7; Yu. L. Spirin & al., Vysokomolek. soyed., 1, 1258 (1959)) the authors explained the peculiarities of the polymerization of non-polar monomers of the above type by the participation of the lithium component, besides the carbanion component, in the growth of the chain. The introduction of 2) to 5) which form complexes with the lithium component of the catalyst, reduces the effect of this component on the growth of the chain. The mechanism of the process is changed correspondingly. It approaches a typical anionic polymerization in the presence of admixtures of high dissolving capacity (THF). The authors presume that the reduction of the activation energy with increasing THF concentration takes place due to the destruction of associates as well as through a change of the complexes between THF and the active centers, and through the increase of the dielectric constant of the medium. In spite of different dielectric constants of ether and dioxane (4.33 and 2.28 at 20°C), the polymerization of styrene in it proceeds at a comparable rate and activation energy. The authors also

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investigated the composition of copolymers in the systems styrene-isoprene and styrene-butadiene in the presence of 2) to 5), and calculated the copolymerization constants for amine and THF. The relative portion of styrene in the copolymer rises in these systems when 2) to 5) are introduced. It may be seen from the data that the effect of the solvents on separate polymerization and copolymerization is not always the same. In the presence of THF, the copolymers are strongly enriched with styrene and correspond to the compositions from typical anionic processes (D. E. Kelley, A. V. Tobolsky, J. Am. Chem. Soc., 81, 1597 (1959)). The relative reactivity of monomers increases in THF, e. g., isoprene < butadiene < styrene. The authors presume that the reactivity of monomers on separate polymerization in polar media is changed in the same sequence as in the case of copolymerization. The effect of solvents 1) to 5) on polymerization largely depends on their electron-donor capacity. Relatively weak electron donors like amine, ether, or dioxane change the polarization of the Li-C bond only slightly. In individual cases, they even increase the activation energy of chain growth as compared with hydrocarbon solvents. The strong electron donors (THF), however, entirely eliminate the effect of lithium. Thus, the polarization

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S/020/61/139/004/019/025

Polymerization of styrene, butadiene ... B103/B206

of the Li-C bond is abruptly increased. The process is here brought nearer to that of typical anionic polymerization, where the carbanion forms the active center. There are 1 figure, 2 tables, and 8 references: 4 Soviet-bloc and 4 non-Soviet-bloc. The most important references to English-language publications see in the body of the abstract.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova
(Physicochemical Institute imeni L. Ya. Karpov)

SUBMITTED: April 24, 1961

Card 6/6

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11.2210

28648
S/020/61/139/006/013/022
B103/B101

AUTHORS: Arest-Yakubovich, A. A., Gantmakher, A. R., and Medvedev, S. S.,
Academician

TITLE: Anionic polymerization in the presence of aromatic compounds

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 139, no. 6, 1961, 1351-1353 X

TEXT: The aim of this article was to find out whether aromatic hydrocarbons participate in an anionic chain growth. The authors found that the anionic polymerization of styrene (in tetrahydrofuran, initiated by sodium-aromatic complexes) is strongly retarded by anthracene. The retardation depends on the ratio of anthracene to styrene. Anthracene exerts an inhibitory effect both if it is added together with the initiator (sodium naphthalene or sodium anthracene) and if a styrene - anthracene mixture is added to "live" polystyrene obtained from sodium naphthalene or sodium diphenyl. The authors conclude that this process takes place with a constant number of active centers. This number is equal to the amount of the initiator used and no chain transfer takes place. Hence, the mentioned retardation is not related to the decrease of the number of

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Anionic polymerization in the presence ... B103/B101

active centers as a result of the shift of the initiation equilibrium of $A^* + C \rightleftharpoons A + C^*$ (II) to the left-hand side. A is anthracene and C styrene; the asterisks denote the ion radicals, i. e. the molecules having an excess electron. Hence, the excess electrons completely pass from anthracene into styrene. The lacking of A^* in the system was also spectrophotometrically confirmed. The complete consumption of A^* is explained

by an irreversible consumption of C^* as a result of the reaction with the monomer and of recombination. Also the low monomer consumption in the initial stage which results from an abrupt retardation of the growth reaction in the presence of anthracene contributes to this effect. This retardation is probably related to the participation of anthracene in growth processes. It is assumed that a joint polymerization of anthracene and styrene takes place since anthracene is very active in the radical reactions. Publications contain no data on the participation of anthracene in anionic copolymerization. The kinetic effects observed by the authors justify the assumption that anthracene adds to the carbanions of styrene thus forming a rather stable and little active anion since the charge is considerably delocalized. This assumption was confirmed

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Anionic polymerization in the presence ... B103/B101

experimentally. An amount of anthracene that was three times higher than the number of active centers was added to a solution of "live" polystyrene (obtained with sodium naphthalene). The electron spectra showed that anthracene copolymerizes with styrene. In contrast to ordinary "live" polymer whose spectrum is essentially changed already one day after the production, the spectrum of the polymer produced from anthracene remains practically unchanged for three days. The shift of the maximum can be explained either by the complex formation between anthracene and the active centers of polymerization which takes place according to M. Levy (Ref. 7, see below) or the shifted maximum 445 m μ corresponds to the anthracene carbanions at the ends of the polymer chains. Large amounts of naphthalene (up to 50% as referred to styrene) influence neither the reaction rate nor the molecular weight. However, they essentially change the spectrum of the "live" polymer. The maximum at 340m μ disappears while maxima at 430 and 550 m μ reappear. The polymer is capable of absorbing further monomer portions while keeping its changed spectrum. The polymerization of a less active monomer as, e. g., butadiene, is more strongly inhibited by anthracene. Thus, anionic polymerization of butadiene at 20°C practically stops already at an anthracene-to-butadiene

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Anionic polymerization in the presence ... B103/B101

ratio of 1 : 30. It is concluded from the spectral data that "live" polybutadiene reacts with anthracene in the same way as "live" polystyrene. There are 2 figures and 11 references, 3 Soviet and 8 non-Soviet. The two most important references to English-language publications read as follows: Ref. 1: M. Szwarc, M. Levy, R. Milkovich, J. Am. Chem. Soc., 78, 2656 (1956); Ref. 7: M. Levy, F. Cohen-Bosidan, Polymer, 1, 517 (1960).

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova
(Physicochemical Institute imeni L. Ya. Karpov)

SUBMITTED: May 18, 1961

Card 4/4

15 9101

29012

S/020/61/140/004/013/023

B106/B110

AUTHORS: Zabolotskaya, Ye. V., Khodzhemirov, V. A., Gantmakher, A. R.,
and Medvedev, S. S., Academician

TITLE: Polymerization and copolymerization of isoprene under the
action of $\alpha\text{-TiCl}_3\cdot\text{Al}(\text{C}_2\text{H}_5)_3$

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 140, no. 4, 1961, 825 - 828

TEXT: The authors studied the kinetics of polymerization of isoprene alone and together with styrene under the action of titanium trichloride and triethyl aluminum. To prevent precipitation of the polymer, benzene was used as solvent. Polymerization was carried out dilatometrically. The components were dosed in analogy with data in Ref. 1 (Ye. V. Zabolotskaya, A. R. Gantmakher, S. S. Medvedev, Vysokomolek. soved., 2, No. 8, 1213 (1960)). All kinetic data were determined at 75°C , the degree of conversion did not exceed 10% by weight. Viscosity, molecular weights, and compositions of polymers were determined in dry argon atmosphere. The average-weight molecular weights (M_w) were measured by the light scattering method, the average-number molecular weights (M_n) by the osmotic method.

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B106/B110

The compositions of copolymers were determined by IR spectroscopy. The authors thank N. V. Makletsova and A. P. Golovina for measuring the molecular weights, and N. V. Desyatova for carrying out the spectrometric measurements. When studying the polymerization of isoprene, polymerization rate and titanium chloride concentration per unit volume were found to be linearly dependent. This indicates that the number of active centers is determined by the concentration of the $\text{TiCl}_3 \cdot \text{Al}(\text{C}_2\text{H}_5)_3$ complex on the surface of TiCl_3 . All experiments were performed with TiCl_3 of a medium grain size of $1.5\text{--}2\mu$. The relation between polymerization rate and monomer concentration, however, is not linear, polymerization rate increases more slowly than isoprene concentration. Polymerization probably takes place on the catalyst surface via complex formation of the monomer with the titanium component of the catalyst, and subsequent penetration of a polarized monomer into the Al-C bond. The total activation energy of polymerization was determined to be 13 kcal/mole from the temperature dependence of the polymerization rate of isoprene at $60\text{--}95^\circ\text{C}$. Table 1 shows the results of molecular weight determinations. The ratio M_w/M_n is close to unity, which indicates that the resultant

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Polymerization and copolymerization ...

polyisoprene exists in the monodisperse phase. The molecular weight depends slightly on the monomer concentrations. When studying the copolymerization of isoprene and styrene, the composition of copolymers and the polymerization rate were determined as a function of the composition of the initial mixture (Figs. 2, 3). It may be seen from Fig. 2 that the copolymers are considerably enriched in isoprene as compared with the composition of the initial mixture. Fig. 3 shows that the rate of copolymerization is much lower than the rates of separate polymerizations of isoprene and styrene. The inhibitory effect of isoprene is particularly high if it is added to styrene in small quantity. The inhibitory effect is due to the reduced reaction rate when a polarized monomer enters the Al-C bond of the transition complex of the chain with the catalyst. This decrease in rate takes place when the styrene molecule in the end group of the chain is replaced by isoprene. It was found that the molecular weights of polymers vary cymbately with a change in polymerization rate at different compositions of the initial mixture (comparison of data from Table 1 with Fig. 3). There are 3 figures, 1 table, and 8 references: 3 Soviet and 5 non-Soviet. The three references to English-language publications read as follows: J. Still, Chem. Rev., 58, 541

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29012

Polymerization and copolymerization ...

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B106/B110

(1958); G. Natta, J. Pasquon, *Advances in Catalysis*, **11**, 68 (1959); N. G. Gaylord, *Trans. N. Y. Acad. Sci.*, **22**, No 6, 387 (1960).

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: May 29, 1961

Table 1. Molecular weights of polymers (the molecular weight of polystyrene is of the order of 10^6 (Ref. 1)).
Legend: (1) moles/liter; (2) moles/liter·min; (3) isoprene in the initial mixture, mole%; (4) molecular weight· 10^{-3} .

[C ₆ H ₆], мол/л ①	[C ₆ H ₆], мол/л ①	[Al(C ₂ H ₅) ₃], ·10 ³ , мол/л ①	TiCl ₄ ·10 ³ , мол/л ①	V·10 ³ , мол л·мин ②	Изопрен в исходн. смеси, мол.% ③	[η]	④ Мол. вес·10 ⁻³	
							M _w	M _n
0.97	—	3.62	3.83	—	100	2.15	500	500
1.03	—	3.72	3.82	—	100	2.25	700	690
1.35	0.66	3.84	3.17	11.8	67.2	2.30	—	600
0.95	1.01	3.58	3.22	5.2	48.5	2.00	—	375
0.41	3.60	4.26	5.96	—	13.0	2.00	—	385

Table 1

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34986

S/190/62/004/003/006/023
B110/B14411. 2210
5.3830AUTHORS: Basova, R. V., Gantmakher, A. R.TITLE: Polymerization of unsaturated compounds in the presence of
K metal and organopotassium compounds in hydrocarbon mediaPERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 3, 1962,^{Mr}
361-365 (MIRA 15:3)

TEXT: The authors studied the separate and joint polymerization of styrene (I), isoprene (II), butadiene (III), and α -methyl styrene (IV) in the presence of K metal and organopotassium compounds in hydrocarbons. In separate polymerization, chain transfer was studied in the presence of hydrocarbons with different proton donor properties. According to P. P. Shorygin (Issledovaniya v oblasti metalloorganicheskikh soyedineniy natriya (Studies in the field of organometallic Na compounds), M. 1910) the reaction $\sim R'K + RH \rightarrow \sim R'H + RK$ (1) takes place, with R' = the polymer carbanion, and RH = hydrocarbon. Whether transfer, degenerate transfer, on chain rupture take place depends on the acidity of RH and stability of R . With the exception of IV, 100% conversion was reached. Polymerization

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Polymerization of unsaturated ...

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of I in toluene and benzene yielded polystyrenes having molecular weights of 135,000, and 350,000. It was polymerized in benzene, cumene, isobutylene, and toluene, metallization of which increases in the given order. The copolymerization of I, II, and III (ratio 1 : 1) in hydrocarbons, with a conversion of $< 30\%$ at 0°C , was initiated by benzyl potassium. Refractometric and infrared spectroscopic studies revealed decreasing activity in the monomer sequence I>III>II. Since the K-R bond is more polar than the Na-R and Li-R bonds, the polymerization with organopotassium compounds is similar to anion polymerization, even in a hydrocarbon medium. In the presence of K metal there are much more anion than radical reactions, since the I-II copolymer obtained with benzyl potassium contains more I than that obtained with K metal. The polymerization of III in benzene, initiated by K metal, yielded colored, highly viscous polybutadiene. When using cumene, the solutions remained intensively colored, and the molecular weight was constant. The drop in molecular weight was smaller on transition from benzene into toluene (362,000 \rightarrow 41,700) since polybutadiene carbanion is likely to be more stable than polyisoprene carbanion. Benzyl potassium initiates the polymerization of the more active butadiene with formation of high-molecular potassium polybutadiene. Degenerate transfer, metallization of the CH_3 group of IV, and formation

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Polymerization of unsaturated ...

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of a stable carbanion took place even in the presence of toluene. The capability of toluene of active chain transfer in the polymerization of II and III is due to the lower stability of polyisoprene and polybutadiene carbanions toward benzyl carbanions. The polymerization of nonpolar monomers in hydrocarbons, initiated by Na and Li metals, is no anion polymerization and causes no chain transfer. There are 2 tables. The most important reference to English-language publications reads as follows: A. A. Morton, M. L. Brown, J. Amer. Chem. Soc., 69, 160, 1947. X

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: February 18, 1961

Card 3/3

37435

S/190/62/004/005/011/026
B110/B144

52230

AUTHORS: Solovykh, D. A., Arest-Yakubovich, A. A., Gantmakher, A. R.,
Medvedev, S. S.

TITLE: Polymerization of styrene and butadiene initiated by sodium
naphthalene in weakly polar media

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 5, 1962,
702-703

TEXT: The activation energy and rate constants of the homogeneous polymerization of styrene and butadiene with organosodium initiators in hydrocarbon media in the presence of small tetrahydrofuran additions were determined for the first time by a two-stage method. First, "live" polymers were obtained by preliminary polymerization of $\sim 1/6$ of the monomer with sodium naphthalene in a tetrahydrofuran medium, and were then used as polymerization initiators in toluene or cumene with tetrahydrofuran. The polymerization rate was measured between -60 and -35°C and the initiator concentration was determined from $c = 2m/M$, where m is the amount of polymerized monomer in g, c is the number of initiator moles, and M is the

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Polymerization of styrene and ...

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molecular weight of the polymer. Toluene caused chain transfer during butadiene polymerization with 6.5% tetrahydrofuran. The polymerization rate of styrene and butadiene in toluene was found to increase with transition from organolithium to organosodium initiators. There is 1 table.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova
(Physicochemical Institute imeni L. Ya. Karpov)

SUBMITTED: March 31, 1961

Card 2/3

15.8610

AUTHORS:

40567
S/020/62/146/002/009/013
B101/B144
Spirin, Yu. L., Gantmakher, A. R., Medvedev, S. S.,
Academician

TITLE:

Association of organolithium compounds and its role during
polymerization

PERIODICAL:

Akademiya nauk SSSR. Doklady, v. 146, no. 2, 1962, 368-371

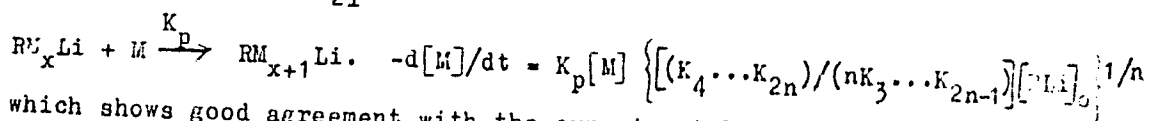
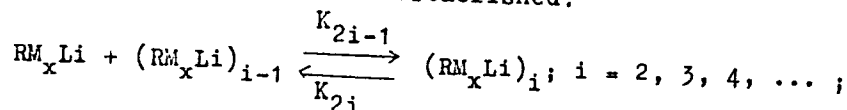
TEXT: When polymerization is initiated by organolithium compounds, the polymerization rate increases more slowly than the concentration of the initiator, owing to deactivation of the active centers by association. The authors studied the effect of the polymer carbanion structure on the association degree during the polymerization of styrene, isopropene, or butadiene initiated by ethyl lithium. The shift of the absorption band toward greater wave lengths and the change in optical density of the band were observed in order to study the conversion of ethyl lithium into associates with the polymer carbanion. The specific effect of the polymers was found to be an increase in initiation rate following the sequence isoprene < butadiene < styrene. An examination of the equation

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Association of organolithium ...

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B101/B144

$-d[M]/dt = K[M][LiR]^{1/n}$ (1), $n > 1$ for chain propagation showed that n depends on the carbanion structure. For polystyrene $n \approx 2$, for polyisoprene $n \approx 3 - 4$, and for polybutadiene $n \approx 5 - 6$. The following reaction for chain propagation is established:



which shows good agreement with the experimental equation (1). The slight change in activation energy brought about by changing the initiator concentration approximately the 10^3 -fold, proves the stability of the associates and the constancy of their composition. The active centers were mainly in an associated state even at an ethyl lithium concentration of 10^{-5} moles/l. There are 3 figures and 1 table. The most important English-language references are: F. Welch, J. Am. Chem. Soc., 81, 1345 (1959); D. I. Worsfold, S. Bywater, Canad. J. Chem. 38, 1891, (1960).

Card 2/3

Association of organolithium ...

S/020/62/146/002/009/013
B101/B144

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-
chemical Institute imeni L. Ya. Karpov)

SUBMITTED: May 31, 1962

Card 3/3

MEDVEDEV, S.S., GANTMAKHER, A.R.

Concerning the directed growth of chains in the process of anionic-coordination polymerization.

Report submitted for the International Symposium of Macromolecular chemistry
Paris, 1-6 July 63

L 16985-63

Pr-4 RM/WW/JD

EPR/EWP(j)/EPF(c)/EWP(g)/EWT(m)/BDS
S/020/63/149/005/009/018

AFETG/ASD PB-4/Pe-4/

AUTHOR:

Basova, R. V., Arest-Yakubovich, A. A., Solovykh, D. A.,
Desyatova, N. V., Gantmakher, A. R., and Medvedev, S. S.

TITLE:

Polymerization of butadiene in the presence of alkali metals
and their compounds in different media

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 149, no. 5, 1963, 1067-1070

TEXT: Literature on the polymerization of dienes, initiated by alkali metals and their compounds, notes that the proportion of structures characteristic of the anion type of polymerization, contrary to expectations, decreases with increasing polarity of the Me-R bond (Me -- alkali metal) in hydrocarbon media. The authors of this work, devoted to investigation of the effect of polymerization conditions on the structure of butadiene, pay special attention to this problem. The investigation was performed under vacuum conditions, with prior thorough cleaning of monomers and solvents. The results obtained show that the increase in the proportion of 1,2-structures of polybutadiene and 3,4-structures of polyisoprene, observed upon transition from potassium to sodium compounds in a hydrocarbon medium is due to the presence of impurities solvating the opposite-charged ions. There are 2 tables.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpev)

Card 34

SUBMITTED: January 10, 1963

POLYAKOV, D.K.; SPIRIN, Yu.L.; GANTMAKHER, A.R.; MEDVEDEV, S.S., akademik

Nature of carbon - alkali metal bond studied by means of electron
absorption spectra. Dokl. AN SSSR 150 no.5:1051-1054 Je '63.
(MIRA 16:8)

1. Fiziko-khimicheskiy institut im. L.Ya.Karpova.
(Chemical bonds) (Carbanions--Absorption spectra)

ACCESSION NR: AP4009149

S/0190/64/006/001/0076/0020

AUTHORS: Zabolotskaya, Ye. V.; Khodzhenirov, V. A.; Gontmakher, A. R.; Kedvedev, S. S.

TITLE: Polymerization and copolymerization of isoprene in the presence of α - TiCl_3 - $\text{Al}(\text{C}_2\text{H}_5)_3$

SOURCE: Vy*sokomolekulyarny*ye soyedineniya, v. 6, no. 1, 1964, 76-80

TOPIC TAGS: polymerization, copolymerization, isoprene, styrene, catalyst, alpha titanium trichloride, triethyl aluminum, polymerization rate, copolymerization rate, activation energy

ABSTRACT: The polymerization of isoprene and its copolymerization with styrene were conducted in benzene, in the presence of α - TiCl_3 - $\text{Al}(\text{C}_2\text{H}_5)_3$. The work was done at 75C, and the extent of polymerization did not exceed 10%. The polymers were reprecipitated by methanol and subjected to chemical analysis, determination of viscosity, molecular weight, and infrared spectroscopy. When 0.97-3.03 Mol/liter concentrations of isoprene (constant amount of catalyst) were tested, it was observed that the molecular weights of the obtained polymers were independent of the

Card

1/2

ACCESSION NR: AP1009149

isoprene concentration, and that the increase in polymerization rate was not proportional to the concentration of the monomer. But the polymerization rate of isoprene proved to be proportional to the amount of $TiCl_3$, as is also the case with styrene and the olefines. Within a temperature range of 60-95C the yield of the polymer increased with the temperature. The overall activation energy of isoprene polymerization was estimated as 13 ± 0.5 Kcal/Mole. The copolymerization of isoprene with styrene showed that an 8.5% addition of isoprene had a three- to four-fold lowering effect on the polymerization rate of styrene and on its molecular weight. The copolymers were greatly enriched in isoprene. The addition of styrene to the isoprene monomer lowered the polymerization rate of isoprene more moderately. Thanks are given to N. V. Makletsov and L. P. Golovin for molecular weight determinations, and to N. V. Desyatov for analysis of composition of the polymers. Orig. art. has: 2 tables and 8 charts.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physical-Chemical Institute)

SUBMITTED: 07Aug62

DATE ACQ: 10Feb64

ENCL: 00

SUB CODE: CH

NO. REF SOV: 002

OTHER: 001

2/2

Card

ACCESSION NR: AP4009150

S/0190/64/006/001/0081/0085

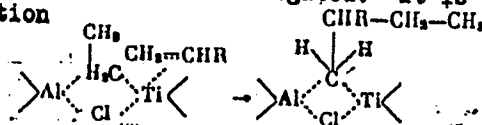
AUTHORS: Zabolotskaya, Ye. V.; Khodzhemirov, V. A.; Gantmakher, A. R.; Medvedev, S. S.

TITLE: Investigation of polymerization mechanism in isoprene with styrene catalyzed by $\alpha - \text{TiCl}_3 - \text{Al}(\text{C}_2\text{H}_5)_3$

SOURCE: Vy*sokomolekulyarny*ye soyedineniya, v. 6, no. 1, 1964, 81-85

TOPIC TAGS: polymerization, styrene, catalyst, isoprene, copolymer chain, monomer, differential composition

ABSTRACT: The mechanism of the $\alpha - \text{TiCl}_3 - \text{Al}(\text{C}_2\text{H}_5)_3$ combination catalyzed polymerization and copolymerization of isoprene and styrene has been investigated. It is assumed that in the primary initiation, the reaction



has no effect on the polymerization rate, and the polymer molecule dimension is limited by the reaction break-off of molecular chains. The polymerization rates for

Card 1/3

ACCESSION NR: AP4009150

styrene and isoprene then yield respectively $V_A = k_{A \cdot A} \cdot a_A$ The rate constant k_{BB}

$$V_B = k_{B \cdot B} \cdot a_B$$

of isoprene molecule transition is determined from the catalytic complex to the copolymer chain as $4.15 \times 10^{-2} \text{ min}^{-1}$. From differential rate equations describing the entry of each monomer (styrene A, isoprene B) into a copolymer, equations of differential composition of the polymer for each monomer are derived

$$\frac{dA}{dB} = \frac{[A]}{[B]} \frac{k_{A \cdot A} \cdot k_A [A]}{k_{B \cdot B} \cdot k_B [B] + 1}, \text{ from which copolymerization constants } r_A \text{ and } r_B \text{ are}$$

determined as being 0.1 and 6.0, respectively. It has been shown that inhibition of styrene polymerization by small isoprene additions is due to a decrease in styrene molecule addition rate to the end of the polymer chain when this unit is an isoprene rather than a styrene residue. Orig. art. has: 16 formulas, 1 figure, and 1 table.

ASSOCIATION: Fiziko-khimicheskii institut im. L. Ya. Karpova (Physicochemical Institute)

Card 2/3

ACCESSION NR: AP4009150

SUBMITTED: 07Aug62

SUB CODE: OC

DATE ACQ: 10Feb64

NO REF SOV: 004

ENCL: 00

OTHER: 003

Card 3/3

BASOVA, R.V.; GANTMAKHER, A.R.; MEDVEDEV, S.S., akademik

Processes of anion and anion-coordination polymerization as
influenced by the nature of active centers. Dokl. AN SSSR
158 no.4:876-879 O '64. (MIRA 17:11)

1. Fiziko-khimicheskiy institut im. L.Ya. Karpova.

LYUDVIG, Ye.B. GANTMAKHER, A.R.; MEDVEDEV, S.S., akademik

Mechanism of cationic polymerization in the presence of metal
halides. Dokl. AN SSSR 156 no. 5:1163-1166 Je '64.
(MIRA 17:6)

1. Fiziko-khimicheskiy institut im. L.Ya.Karpova.

1 16327-65 EWT(m)/EPF(c)/EWP(j)/T Pt-4/P1-4 RM
ACCESSION NR: AP4049153 S/0190/64/006/011/2030/2034

AUTHOR: Rozenberg, B. A.; Chekhuta, O. M.; Lyudvig, Ye. B.; Gantmakher, A. R.;
Medvedev, S. S. B

TITLE: Kinetics and equilibrium of the polymerization of tetrahydrofuran induced by tri-
alkyloxonium salts

SOURCE: Vy*sokomolekulyarny*ye soyedineniya, v. 6, no. 11, 1964, 2030-2034

TOPIC TAGS: trialkyloxonium, tetrahydrofuran, block polymerization, solution polymeri-
zation, tetrafluoroborate, cationic polymerization

ABSTRACT: The kinetics of the polymerization of tetrahydrofuran, both in block and in
solution in diethyl ether, under the influence of triethyloxonium tetrafluoroborate was in-
vestigated by a dilatometric method. The characteristics of the catalyst and the initial
substances are given. The kinetic curves at different initial catalyst concentrations are
given, showing that the rate of polymerization is directly proportional to the concentration
of catalyst and is described by the equation $d[M]/dt = k_p[C_0]([M] - [M_0])$. The rate con-
stant of the polymerization at 20°C determined from the experimental data is equal to 1.66×10^{-2} liter/mole. sec. A study of the effect of the catalyst concentration on the molecular

Card 1/3

L 16327-65

ACCESSION NR: AP4049153

weight of the forming polymer showed that over the concentration range 0.02-0.08 mole/liter the molecular weight is inversely proportional to the catalyst concentration. Tabulated data show that at a constant concentration of catalyst (0.02 mole/liter), the molecular weight increases with increasing amount of polymerized monomer. Over a temperature range of 0-40C, the rate of polymerization, the equilibrium state and the molecular weight were found to be highly dependent on temperature. From the temperature dependence of the rate constant, the energy of activation was $E=13.3$ kcal/mole and the preexponential factor $A=1.64 \times 10^{-8}$ liter/mole. sec. The molecular weight decreased considerably with increasing temperature. The equilibrium concentration of the monomer during polymerization was independent of the initial concentrations of catalyst and monomer and depended only on the temperature. On the basis of this correlation, the change in enthalpy and entropy of polymerization was calculated: $\Delta H = -5.5$ kcal/mole; $\Delta S = -20.8$ cal/mole. deg. The limiting temperature of block polymerization calculated by the equation $T_c = \Delta H / \Delta S^\circ + R \log [M_p]$ is 73C. Orig. art. has: 6 figures, 1 table and 1 formula.

ASSOCIATION: Donetskoye otdeleniye instituta organicheskoy khimii AN USSR (Donetsk Division of the Institute of Organic Chemistry, AN Ukr. SSR); Fiziko-khimicheskiy institut im. L. Ya. Karpova (Institute of Physical Chemistry)

Card

2/3

L 16327-65
ACCESSION NR: AP4049153

SUBMITTED: 23Jan64

ENCL: 00

SUB CODE: OC

NO REF SOV: 003

OTHER: 018

Card 3/3

L 16326-65 EWT(m)/EPF(v)/EWF(j)/T P-4/P1-4 RM
 ACCESSION NR: AP4049154 S/0190/64/006/011/2035/2039

AUTHOR: Rozenberg, B. A.; Lyudvig, Ye. B.; Cantmakher, A. R.; Medvedev, S. S. B

TITLE: Mechanism of the induced polymerization of tetrahydrofuran induced by trialkyloxonium salts

SOURCE: Vy*sokomolekulyarny*ye soyedineniya, v. 6, no. 11, 1964, 2035-2039

TOPIC TAGS: tetrahydrofuran, boron fluoride etherate, epichlorohydrin polymerization, living polymer, polytetramethylene oxide, trialkyloxonium salt, tetrahydrofuran polymerization, cationic polymerization

ABSTRACT: The mechanism of the cationic polymerization of tetrahydrofuran was investigated and the peculiarities of the polymerization induced by trialkyloxonium salts were discussed on the basis of the given reaction mechanisms. By the analytical method used, it was found that the initiation of the polymerization of tetrahydrofuran in the presence of the system boron fluoride etherate + epichlorohydrin proceeds with the formation of distinct ion pairs and an internal oxonium salt. The peculiarity of the tetrahydrofuran polymerization is that, in contrast to the cationic polymerization of vinyl compounds, the growing ion is oxonium and not carbon. Infrared spectra show the complete absence of

Card 1/3

L 16326-65

ACCESSION NR: AP4049154

lateral methyl groups in the polytetramethylene oxide molecule. On the basis of an analysis of the experimental data, it was established that the polymerization of tetrahydrofuran induced by trialkyloxonium salts proceeds without the rupture of the reaction chains and with the formation of "living polymers." The effect of small additions of water on the polymerization was also studied and water was found to be the chain transfer agent. Its addition does not affect the rate of polymerization, but decreases the molecular weight. The molecular weight also decreases with increasing temperature of polymerization, but the decrease in molecular weight is determined not by the decrease in the ratio between the rate constant of chain growth and the rate constant of chain rupture, as in the cationic polymerization of unsaturated compounds, but by the decrease in the equilibrium monomer concentration of the monomer with increasing temperature. On the basis of the equilibrium monomer concentration, the rate constant of the reversible reaction was calculated as $k_d = 4.67 \times 10^{-2} \text{ sec}^{-1}$ (at 20°C). From the temperature dependence of this constant, the activation energy and the preexponential factor of the depolymerization reaction determined from this relationship are $E=19.4 \text{ kcal/mole}$ and $A=1.65 \times 10^{13}$. It was found that the molecular weights of polytetramethylene oxide are in disagreement with the values expected according to the M/C theory. Orig. art. has: 2 figures, 1 table and 13 formulas.

Card 2/3

L 16326-65
ACCESSION NR: AP4049154

2
ASSOCIATION: Donetskoye otdeleniye instituta organicheskoy khimii AN USSR (Donetsk
Division of the Institute of Organic Chemistry, AN Ukr. SSR); Fiziko-khimicheskiy institut
im. L. Ya. Karpova (Institute of Physical Chemistry)

SUBMITTED: 23Jan64

ENCL: 00

SUB CODE: OC

NO REF SOV: 002

OTHER: 012

Card

3/3

L 56067-65 EWT(m)/EPF(c)/EWP(j)/T Pc-4/Pr-4 RM

ACCESSION NR: AP5018555

UR/0020/64/158/004/0876/0879

AUTHOR: Basova, R. V.; Gantmakher, A. R.; Medvedev, S. S. (Academician)

TITLE: Influence of the nature of the active sites on processes of anionic and anionic-coordination polymerization

SOURCE: AN SSSR. Doklady, v. 158, no. 4, 1964, 876-879

TOPIC TAGS: polymerization, organopotassium compound, monomer

Abstract: The influence of the nature of the monomer and the medium on the structure and properties of the active sites in polymerization initiated by organopotassium compounds was studied. The kinetics of the polymerization of alpha-methylstyrene, styrene, isoprene, and butadiene was investigated, both in hydrocarbon medium (benzene, toluene, cumene) and in the presence of additions of tetrahydrofuran (0.5 to 50%) at various temperatures (-50° to +30°), by a dilatometric method, and the molecular weights of the corresponding polymers were determined. Organopotassium compounds synthesized in hydrocarbon medium (1,2) or in tetrahydrofuran medium (3,4) were used in initiators: 1) benzyl-potassium; 2) low-molecular dipotassiumpoly-alpha-methylstyrene; 3) potassium naphthalene; 4) dipotassium tetramer of alpha-methylstyrene. The activity of the monomers increased in the sequence: alpha-methylstyrene < isoprene <

Card 1/2

L 56067-65

ACCESSION NR: AP5018555

< butadiene < styrene. The rate of the initiation of polymerization of various monomers in hydrocarbon medium at 0° in the presence of benzylpotassium increased with increasing activity of the monomers in the sequence isoprene < butadiene < styrene; in the case of dipotassium poly-alpha-methylstyrene, a compound with a less stable carbanion, even the polymerization of isoprene took place without an induction period. In the polymerization of alpha-methylstyrene with organopotassium compounds in a mixture of cumene or toluene with tetrahydrofuran (~50%), even at 50°, the molecular weight of poly-alpha-methylstyrene was lower than expected, indicating the presence of a reaction of chain transfer through the monomer. Orig. art. has 1 graph and 1 table.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physicochemical Institute)

SUBMITTED: 25May64

ENCL: 00

SUB CODE: 03, GC

NO REF SOV: 004

OTHER: 001

JPRS

Card 2/2

PIITAKOV, S.A.; GROMOV, V.I.; P. GROMOV, S.A.

Effect of the association of organolithium compounds on their
ultraviolet spectra. Vysokomol.soi. 7 no.1:181 Ja '65.

(MIRA 18:5)

ROZENBERG, B.A.; LYUDVIG, Ye.B.; GANTMAKHER, A.R.; MEDVEDEV, S.S.

Effect of reaction chain transfer to polymer in the cationic
polymerization of oxygen-containing cyclic compounds. *Vysokom.*
soed. 7 no.1:188-189 Ja '65. (MIRA 18:5)

LAUTING, Y.G.; RUPPENHAG, B.A.; SIVILEVA, T.A.; GINTALIS, A.F.;
MEIVEREV, S.S.

Polymerization of tetrahydrofuran in the presence of antimony
pentachloride and its compounds. Vysokom. soed. 7 no.2:269-271
P 165. (1964 18:3)

1. Fiziko-khimicheskiy institut imeni Karpova, Moskva i Donetskiiy
filial Instituta khimicheskikh reaktivov i osobo chistykh veshchestv.

LANOVSKAYA, L.M.; MAKLETSOVA, N.V. [deceased]; GANTMAKHER, A.R.;
MEDVEDEV, S.S.

Polymerization of ethylene in the presence of various composite
catalysts based on $TiCl_3$. Vysokom. soed. 7 no.4:741-746 Ad '65.

Nature of the active centers in the processes of polymerization
in the presence of composite catalysts based on $TiCl_3$. Ibid.:
747-750

(MIRA 18:6)

1. Fiziko-khimicheskii institut imeni Karpova, Moskva.

PRONINA, I.A.; SPIRIN, Y.I.; BLAGONRAVOVA, A.A.; AREF'YEVA, S.M.; GANTMAKHER, A.R.; MEDVEDEV, E.S., akademik

Mechanism underlying the catalytic action of Co^{2+} compounds in the urethane-forming reaction. Dokl. AN SSSR 161 no.2:362-365 Mr '65.
(MIRA 18:4)

1. Gosudarstvennyy nauchno-issledovatel'skiy i proyektnyy institut lakokrasochnoy promyshlennosti i Fiziko-khimicheskiy institut im. L.Ya.Karpova.

GUTMAN, P.I.

Sur la representation canonique de substitutions isomorphiques d'un groupe semi-simple complexe de Lie. C.R. Acad. Sci., 207(1938), 208-210.

Canonical representation of automorphisms of a complex semi-simple Lie group. Matem. sb., 5(47), (1939), 101-146.

On the classification of real simple Lie groups. Matem. sb., 5(47) (1939), 217-250.

O trokhchlennykh Prostikh podgruppakh poluprostykh grupp Lie. M., referaty AN, fiz.-matem. OTD. (1940).

Ob odnom spetsial'nom klasse determinantov v svyazi s integral'nyimi yadrami Kellog'a. Matem. sb., 42(1935). 531-500.

Kalgebraicheskomu analizu metoda idak. A.M. Krylova preobrazovaniya vekovogo uravneniya. L., Trudy vtorogo vseroyuzn. Matem. s'ezda, T. 2(1936), 45-46.

SO: Mathematics in the USSR, 1917-1947

edited by Kurosh, A.G.,

Markushevich, A.I.

Rashevskiy, P.I.

Moscow-Leningrad, 1946.

GANTMAKHER, F.R.

Gantmacher, F. R., and Levin, L. M. Equations of motion of a rocket. Appl. Math. Mech. [Akad. Nauk SSSR. Prikl. Mat. Mech.] 11, 301-312 (1947). (Russian. English summary)

A rocket consists of three parts: (i) metallic components which remain unaltered during flight, (ii) a propellant which is consumed during the burning period and (iii) burning gases in the interior of the body. Eventually these gases pass out through the exit plane of the nozzle and are then no longer considered to form part of the body; while in the body their mass is negligible in comparison with the total mass, but they possess a high velocity relative to the parts (i) and (ii). By considering the linear and angular momentum of the systems S and Σ which consist of those parts of the rocket which at some fixed instant of time t belong respectively to (i), (ii) and (i), (ii), (iii), the authors derive

the equations of motion of a rocket. In investigations of this type the chief difficulties arise from the fact that the familiar dynamical principles, which have been established by applying Newton's laws to rigid bodies of constant mass, are not necessarily true for systems of changing mass content. The equations as first obtained depend upon three general groups of forces, namely: (a) external forces due mainly to the pressure of the air, (b) forces due to the reaction caused by the ejected gases and (c) Coriolis forces. The latter two groups are then investigated in greater detail and are expressed in terms of the rate of ejection of the gases from the burning charge surface and from the nozzle, the variation in density, the angular velocity and other parameters. The velocity of the centre of gravity relative to the body is also found and Euler's equations for the angular motion about the principal axes of inertia are derived and modified so as to allow for the rotation of these axes inside the rocket.

R. A. Rankin (Cambridge, England).

Source: Mathematical Reviews, 1948, Vol 9, No. 3

So: AERONAUTICAL Sci. and AVIATION IN THE
SOVIET UNION, L.C. 1955

Spring
1955

GANTMAKHER, F.R.

Gantmacher, F. R., and Levin, L. M. Equations of motion
of a rocket. Tech. Memos. Nat. Adv. Comm. Acad. Sci.
no. 1255, 21 pp. (1950).

Translated from Appl. Math. Mech. [Akad. Nauk SSSR
Prikl. Mat. Mech.] 11, 391-312 (1947); Russ. Rev. 9, 152.

Source: Mathematical Reviews,

Vol. 11, No. 10

SMU

10/15

10/15

GANTMAKHER, F.R.

PHASE II

TREASURE ISLAND BIBLIOGRAPHICAL REPORT

AID 433 - II

BOOK

Authors: GANTMAKHER, F. R. and KREYN, M. G. Call No.: QA263.G3

Full Title: OSCILLATION MATRICES AND KERNELS, AND SMALL OSCILLATIONS
OF MECHANICAL SYSTEMS. 2nd revised edition

Transliterated Title: Ostsillyatsionnyye matritsy i yadra i malyye
kolebaniya mekhanicheskikh sistem. 2-e izd.

Publishing Data

Originating Agency: None

Publishing House: State Publishing House of Technical and
Theoretical Literature

Date: 1950

No. pp.: 359

No. of copies: 4,000

Editorial Staff: The authors have used the valuable remarks made about
the first edition by Doctor V. L. Shmullian of the Academy of Sciences,
killed in World War II.

Text Data

Coverage: The book is divided in five chapters and two appendices, which
include: a general knowledge of the matrix theory and quadratic forms;
theory of oscillation matrices; small oscillations of a mechanical
system of n masses in a linear elastic continuum with reference to
Jacobian matrices; small oscillations of a mechanical system with an
infinite number of degrees of freedom; algebra of matrices with the

1/17

GANTMAKHER, F. R.

PHASE I

TREASURE ISLAND BIBLIOGRAPHICAL REPORT

AID 434 - I

BOOK

Call No.: QA263.G35

Author: GANTMAKHER, F. R.

Full Title: THE THEORY OF MATRICES

Transliterated Title: Teoriya matrity

Publishing Data

Originating Agency: None

Publishing House: State Publishing House of Technical and
Theoretical Literature

Date: 1953

No. pp.: 491

No. of copies: 5,000

Editorial Staff: Faddeyev, D. K., Potapov, V. P., Kotelyanskiy, D. M.,
Kreyn, M. G. and Uzkov, A. I. gave valuable suggestions after
reading the manuscript.

Text Data

Coverage: The book is based on lectures given by the author for 17
years in the State universities of Moscow and Tbilisi, and in the
Moscow Physico-Technical Institute. The author states that there
is no book in Russian and foreign literatures which covers fully
the problems of the theory of matrices and its various applications.
His book fills this gap.

The book is dedicated not only to students in pure mathematics, but
also to specialists in connected fields (physicists and engineers).

1/5

Teoriya matrits

AID 434 - I

Higher mathematical knowledge is a prerequisite. Constant references in the text and in footnotes to the original sources give a sound basis to the author's statements.

In analyzing this book the text was compared with the following English texts:

- Linear Algebra and Matrix Theory (1952) by R. R. Stoll
- Lectures on Matrices (1934) by J. H. M. Wedderburn
- The Theory of Determinants, Matrices and Invariants (1928) by H. W. Turnbull
- Introduction to the Theory of Canonical Matrices (1932) by H. W. Turnbull and A. C. Aitken
- The Algebra of Vectors and Matrices (1951) by T. L. Wade
- Vectors and Matrices (1943) by C. C. MacDuffee
- The Theory of Matrices (1933) by C. C. MacDuffee
- Operational Methods in Applied Mathematics (1948) by H. S. Carslaw and J. C. Jaeger
- An Introduction to Probability Theory (1950) by W. Feller

The book may be regarded as a fundamental text in the matrix theory. Its value is in the comprehensive accumulation of practically everything, previously widely dispersed, pertaining to matrices and their

2/5

Teoriya matrits

AID 434 - I

applications to other branches of science (e.g., theory of probability, oscillation theory, stability of motion, etc.). A characteristic of the book is its laconicism in the deductions of the formulae and the absence of some detailed definitions, which usually form an integral part in the available English texts selected for comparison and mentioned above. This can be explained by the fact that this is an advanced course. The book appears to be a good reference book, well planned and written.

TABLE OF CONTENTS is presented here in abbreviated form: only the titles of the chapters are mentioned and under them only the items not found in the English texts or pertaining to Russian authors are cited.

Introduction	PAGES
PART I. FUNDAMENTALS OF THE THEORY	7-10
Ch. I Matrices and Operations with Them	11-27
Ch. II Gauss Algorithm and Its Applications	28-48
Ch. III Linear Operators in a n -Dimension Vector Space	49-68
Ch. IV Characteristic and Minimum Matric Polynomials	69-82
Generalization of Bézout theorem (p. 72). The method of	
D. K. Faddeyev of simultaneous calculation of coefficients	
of the characteristic polynomial and companion matrix (p.77).	

Teoriya matrits

AID 434 - I

PAGES
83-109

- Ch. V Functions of a Matrix
Stability of motion in a linear system (solution of Lyapunov's general problem of stability of motion) (p. 106).
- Ch. VI Equivalent Transformations of Polynomial Matrices. Analytical Theory of Elementary Divisors 110-145
- Ch. VII Structure of a Linear Operator in n -Dimension Space. Geometric Theory of Elementary Divisors 146-177
Method of Academician A. N. Krylov (1937) of determining effectively the minimum polynomial characteristic of a secular-equation (pp. 167-177). Numerical solution of a secular equation was also given by A. M. Danilevskiy in 1937, see Matem. Sborn. 44-2, 1937, 169-172.
- Ch. VIII Matrix Equations 178-198
- Ch. IX Linear Operators in Unitary Vector Space 199-238
- Ch. X Quadratic and Hermitian Forms 239-281
- PART II SPECIAL QUESTIONS AND APPLICATIONS
- Ch. XI Complex Symmetric Matrices, Skew-Symmetric (or Alternate) Matrices, and Orthogonal Matrices 282-299
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Ch. XIII	Matrices with Non-Negative Elements	PAGES
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	Lyapunov's transformation (p. 374). Canonical form of a reducible (Lyapunov's) system. Yerugin theorem (p.378), I. A. Lappo-Danilevskiy's application of the theory of analytical functions of many matrices to the study of differential systems in the vicinity of a singular point: (pp. 415-418).	371-418
Ch. XV	Routh-Hurwitz Problem and Connected Questions	419-480
	Literature	481-487
	Subject Index	488-491

Purpose: The book is dedicated not only to mathematicians (students, aspirants, scientific workers), but also to specialists (physicists, research engineers) interested in applied mathematics.

Facilities: None

No. of Russian and Slavic References: A total of 210 references is given in the bibliography of which 140 are Russian.

Available: Library of Congress.

GANTMAKHER, F.R.

Letter to the editor of the periodical "Avtomatika i telemekhanika."
Avtom. i tselm. 14 no.1:110-113 Ja-F '53. (MIRA 10:3)
(Automatic control)

USSR/Mathematics - Stability

Card 1/1

Authors : Ayzerman, M. A.; Gantmakher, F. R.

Title : Conditions for the existence of a region of stability for a single-circuit system of automatic regulation

Periodical : Prikl. mat. i mekh., 18, 103-122, Jan/Feb 1954

Abstract : A single-circuit system is described by systems of linear differential equations with constant real coefficients. For each different system, necessary and sufficient conditions are proved for the existence of a region of stability. The basic result of the article is a necessity theorem for a system whose characteristic equation has the form:

$$D^{(1)}(p) + D^{(2)}(p) = 0.$$

Institution : Moscow Physicotechnical Institute, Moscow

Submitted : September 12, 1953

GANTMAKHER, F. R.

USSR/Mathematics - Relay systems

FD-1655

Card 1/1 Pub. 85-7/16

Author : Ayzerman, M. A., and Gantmakher, F. R. (Moscow)

Title : A class of dynamic problems that reduce to the theory of relay systems

Periodical : Prikl. mat. i mekh., Vol. 19, 222-224, Mar-Apr 1955

Abstract : The author studies an oscillatory system described by the following equations: $d_{ij}(p)x_j - M_{1i}z = A_i \sin(\omega t + a_i)$, $z = f(x_k)$ (tensor summation convention applies to repeated indices; $i=1, \dots, n$; $p=d/dt$), where x_j and z are generalized coordinates of the system, $d_{ij}(p)$ are polynomials with real coefficients, ω, M_{1i}, A_i, a_i are given numbers, and function $f(x_k)$ corresponds to one of the graphs shown of step function. He notes that many problems of the theory of oscillations reduce to the determination of the periodic solution of the above system, where self-excited oscillations are represented by all $A_i=0$ and A_i not zero represent forced oscillations in the zone of damping. Ten references (e.g. Ya. Z. Tsypkin, "Forced oscillations in relay systems of automatic regulation," Avtom. i telem., Vol. 13, No 5, 1952; "Stability of periodic regimes in relay systems of automatic regulation," ibid., Vol. 14, No 5, 1954).

Institution : --

Submitted : November 25, 1954

AYZERMAN, M.A.; GANTMAKHER, F.R.

Comment of the article of M.A. Aizerman and F.R. Gantmakher
"Conditions for the existence of a region of stability for a single-
-circuit automatic control system," in FMM vol.18, no.1, '54.
Prikl.mat.i mekh. 20 no.3:447 My-Je '56. (MLRA 9:8)
(Automatic control)

Gantmakher, E. R.

1331. Aizerman, M. A., and Gantmakher, E. R., On the detection of periodic regimes in a nonlinear dynamic system with piecewise linear characteristic (in Russian), *Dokl. Akad. Nauk*, 20, 5, 639-654, 1956.

The system under discussion is

$$\dot{x} = Ax + p(x),$$

where x and A are n -vectors, A is a constant square matrix and p is a scalar function. It is assumed that p is piecewise linear (several pieces) and the calculations are carried out in the obvious and only possible manner. There are 12 references to automatic regulation.

S. Lefschetz, Mexico

Gantmakher, F.R.

Определение Переходных Процессов в Системах с Кусочно-Линейной Характеристикой. Советский Журнал Звукотехники и Телекоммуникации, 1964, № 1, стр. 97-110. На русском. Determination of periodic solutions in systems with a piecewise linear characteristic composed of straight-line pieces. Periodic solutions of corresponding differential equations are found in the form of complete Fourier series without neglecting harmonics.

GANIMAKHER, F.R.

✓ Alzerman, M. A., and Ganimaker, F. R. On the determination of periodic regimes in a non-linear dynamic system with piece-wise linear characteristic. Prikl. Mat. Meh. 20 (1956), 639-654. (Russian)

1-F/W

Approved
MTT

GRANTMAKHER F. R.

Call Nr: AF 1108825

Transactions of the Third All-union Mathematical Congress (Cont.) Moscow,
Jun-Jul '56, Trudy '56, V. 1, Sect. Rpts., Izdatel'stvo AN SSSR, Moscow, 1956, 237 pp.
Vulikh, B. Z. (Leningrad). Semiordered Rings. 20-21

Mention is made of Domrachev, G. I.

There are 2 references, both of them USSR.

Gavrilov, L. I. (Leningrad). K-continued Polynomials. 21

There is 1 USSR reference 21

Grantmakher, F. R. (Moscow). On Structural Lattice
Stability of the Sum of Two Polynomials. 21

Gurevich, G. B. (Moscow). Algebra of a Group of Automorphisms
of an Arbitrary Standard Zero-algebra. 21-22

There are 2 references, both of them USSR.

Zavalo, S. T. (Cherkassy). Operator Free Groups. 22-23
Card 8/80

GANTMAHER, F.R.

AUTHOR AYZERMAN, M.A., GANTMAHER, F.R. (Moscow) PA - 2555
 TITLE Determination of Periodic Solutions in Systems with a
 Straight-Line Characteristic Composed of Line Pieces Parallel
 to two Given Straight Lines. II. (Opredeleniye periodiches-
 kikh rezhimov v sistemakh, soderzhashchekh kusochno-lineyny
 kharakteristik, sostavlennyye iz zven'yev, parallel'nykh
 dvum zadannym pryamym. II, Russian)
 PERIODICAL: Avtomatika i Telemekhanika, 1957, Vol 18, Nr 3, pp 193 - 200
 U.S.S.R.
 Received: 4 / 1957 Reviewed: 6 / 1957
 ABSTRACT: The problems which can be solved according to the method quoted
 in the first part of the paper are generalized in four direc-
 tions in the second part. 1) Complicated processes can be in-
 vestigated in systems with a binary broken characteristic.
 2) Continuous characteristics or characteristics consisting
 of any number of line pieces of different straight lines can
 be investigated on the condition that the angular coefficients
 of the straight lines are equal to one of the two given fac-
 tors k' and k ". 3) Also more general conditions for the trans-
 ition of one characteristic-unit to the other can be examined.
 4) A far more general class of exterior influences (that is of
 the functions $F_j(t)$) can be investigated, in the course of
 Card 1/2 which these functions have to be determined by their Fourier

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Determination of Periodic Solutions in Systems with a
Straight - Line Characteristic Composed of Line Pieces
Parallel to two Given Straight Lines.

series. It is assumed that the period T can be divided into
 N stages and that during each stage the point x_1, y_1 moves
on a straight line that has one of the given directions
determined by the angular coefficients k' and k'' . It is assumed
that for each i -stage ($i = 1, 2, \dots, N$) the equation of the
straight line and the conditions for the conclusion of the stage
are given. The processes are illustrated by three examples.
In the following chapter the equation of the periods in the ge-
neralized problem will be deduced.
(6 illustrations and 2 citations from Slav publications)

ASSOCIATION: Not given
PRESENTED BY:
SUBMITTED 20.6.1956
AVAILABLE: . Library of Congress.

Card 2/2

GANTMAKHER, F. R.

AUTHORS: Ayzerman, M. A., Gantmakher, F. R., (Moscow) 103-11-7/10

TITLE: On Some Peculiarities of Switching Over in Non-Linear Systems of Automatic Control with a Partly Smooth Characteristic of a Non-Linear Element (O nekotorykh osobennostyakh pereklyucheniya v nelineynykh sistemakh avtomaticheskogo regulirovaniya s kusochno gladkoy kharakteristikoy nelineynogo elementa)

PERIODICAL: Avtomatika i Telemekhanika, 1957, Vol. 18, Nr 11, pp. 1017-1028 (USSR)

ABSTRACT: The processes investigated appear as follows: $x_i = \sum_{j=1}^n a_{ij}x_j + \lambda_i y$ ($i=1,2,\dots,n$), $y=f(x)$, $x = \sum_{j=1}^n \beta_j x_j - \kappa y$, where $a_{ij}, \beta_j, \lambda_i$ and κ are numbers (some of them may also be noughts). It is assumed that the characteristic $y=f(x)$ consists of two smooth curves which are called the granches I and II of the characteristic. On these curves the points of convergence P_1 and P_2 are given. If the representing point moves in the plane x,y along one of the branches and reaches the point of convergence at $t = t^*$ transition to the other branch takes place at that moment. This is switching over, which can be continuous or discontinuous.

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On Some Peculiarities of Switching Over in Non-Linear Systems 103-11-7/10
of Automatic Control with a Partly Smooth Characteristic of a Non-Linear
Element.

There is normal and sliding switching over. In the case of the latter, though the point passes over to the other branch, it immediately returns to the old branch in the same moment without moving along the new branch at all. Types of switching over in the case of characteristics consisting of infinite curves as well as of curve sections, and types of switching over in systems with a feedback closed round the non-linear element are investigated. It is shown that, in the case of discontinuous characteristics, also in relay systems, in the case of sliding switching over considerable changes of x during sliding and jumps along the straight line inclined towards the y -axis in the direction of the "lacking characteristic branches" are observed. In practice the type of the sliding switching over realized depends on the small parameters, and the sliding switching over with the above mentioned changes of x and the discontinuities are observed in systems with elastic feedback if their time constant is small. Sliding motions are observed also in the case of continuous but kinked characteristics. In systems with discontinuous characteristics, which are different from relay characteristics, indefinite switching over, i.e. such with dis-

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On Some Peculiarities of Switching Over in Non-Linear Systems 103-11-7/10
of Automatic Control with a Partly Smooth Characteristic of a Non-Linear
Element.

continuities, which, however, cannot be determined by means
of the equations investigated here, can occur. There are 12
figures and 5 Slavic references

SUBMITTED: April 29, 1957.

AVAILABLE: Library of Congress

Card 3/3

GANTMAKHER, F.R.

AUTHOR: AYZERMAN, M.A., GANTMAKHER, F.R. (Moscow) 40-5-7/20

TITLE: The Stability in Linear Approximation of Periodic Solutions of a System of Differential Equations With Discontinuous Right Sides (Ustoychivost' po lineynomu priblizheniyu periodicheskogo resheniya sistemy differentsial'nykh uravneniy s razryvnymi pravymi chastyami).

PERIODICAL: Prikladnaya Mat.i Mekh., 1957, Vol.21, Nr 5, pp.658-669 (USSR)

ABSTRACT: In Lyapunov's classical investigations [Ref.1] the problem of determining stability of periodical solutions of systems of differential equations in noncritical cases could be reduced to the determination of the stability of the zero solution of the linear approximation. Here it must be presupposed that the right sides of the differential equations are analytic functions continuously depending on the arguments in a certain neighborhood. In the present paper the authors give a generalization of Lyapunov's theorems for the case that the right sides possess discontinuities for certain values of the arguments. Here it turns out to be necessary to define more exactly the notion of the linear approximation and to determine what is to be understood by this in the discontinuous case. With the aid of the linear approximation thus defined some theorems are formulated and proved which are completely

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The Stability in Linear Approximation of Periodic Solutions 40-5-7/20
of a System of Differential Equations With Discontinuous Right Sides

analogous to the corresponding stability theorems of Lyapunov. Thus the asymptotic stability and also the instability can be determined from the behavior of the solutions of the linear approximation of the non-linear initial system. There are 4 figures, no tables, and 2 Slavic references.

ASSOCIATION: Moskovskiy fiziko-tekhnicheskii institut (Moscow Physico-technical Institute)

SUBMITTED: May 15, 1957

AVAILABLE: Library of Congress

Card 2/2

$$G \cap N = N \cap H \cap F' \cap K'$$

AUTHOR: AYZERMAN, M.A., GANTMAKHER, F.R.

20-4-1/51

TITLE: Stability After the Linear Approximation of the Periodic Solutions of a System of Differential Equations With Discontinuous Right Sides (Ustoychivost' po lineynomu priblizheniyu periodicheskikh resheniy sistemy differentsial'nykh uravneniy s razryvnymi pravymi chastyami)

PERIODICAL: Doklady Akad. Nauk SSSR, 1957, Vol. 116, Nr. 4, pp. 527-530 (USSR)

ABSTRACT: Given the system

$$(1) \quad \frac{dz_1}{dt} = f_1(z_1, \dots, z_n, t)$$

with the periodic solution $x_1 = \tilde{x}_1(t)$, the period be τ . Let the f_1 be defined in an infinite cylinder with the axis $x_1 = \tilde{x}_1(t)$.

Let the sequence of hyper-surfaces $F_\alpha(z_1, \dots, z_n, t) = 0$ cut C into the regions H_α , $\alpha = 1, 2, 3, \dots$, where the curve $z_1 = \tilde{z}_1(t)$ intersects the surface F_α in the moment $t = t_\alpha$ in H_α and thereby it goes over from the "positive" to the "negative" side of F_α .

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Here the f_i in M_α may have jumps ξ_i^α . Otherwise let the f_i be

Stability After the Linear Approximation of the Periodic Solutions 20-4-1/51
of a System of Differential Equations With Discontinuous Right Sides

continuous in all \bar{H}_α and differentiable (uniformly with respect to t) with respect to z_1, \dots, z_n in the points of the curve $z_i = \tilde{z}_i(t)$ ($t_{\alpha-1} \leq t \leq t_\alpha$). In every domain H_α for given initial conditions let (1) have a unique solution which can be continued to $H_{\alpha+1}$. Let the f_i be periodic in t with the period T . Let F_α be continuous and smooth in M_α , where on one side of the surface $F_\alpha > 0$ and on the other side $F_\alpha < 0$. The hyper surfaces F_α do not intersect each other. The system of linear approximation for (1) with respect to the solution $z_i = \tilde{z}_i(t)$ is defined as follows:

1) let the integral curves of this system be continuous between the planes $t = t_{\alpha-1}$ and $t = t_\alpha$ and there let them satisfy the linear system

$$(2) \quad \frac{dx_i}{dt} = \sum_{j=1}^n \left(\frac{\partial f_i}{\partial z_j} \right)_{z=\tilde{z}(t)} \cdot x_j,$$

where the $\left(\frac{\partial f_i}{\partial z_j} \right)_{z=\tilde{z}(t)}$ are calculated for the values of f_i in H_α .

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Stability After the Linear Approximation of the Periodic Solution 20-4-1/51
of a System of Differential Equations With Discontinuous Right Sides

2) In the points of intersection with the planes $t = t_\alpha$ the integral curves $x_i = x_i(t)$ have jumps which are determined from the linear relations:

$$(3) \quad x_i(t_\alpha+0) - x_i(t_\alpha-0) = \xi_i^\alpha \sum_{j=1}^n h_j^{\alpha-} x_j(t_\alpha-0),$$

where

$$h_j^{\alpha-} = \left[\frac{\partial F_\alpha / \partial z_i}{(dF_\alpha / dt)^-} \right]_{M_\alpha}, \quad \frac{dF_\alpha}{dt} = \sum_{i=1}^n \frac{\partial F_\alpha}{\partial z_i} f_i + \frac{\partial F_\alpha}{\partial t}.$$

Theorem: If under these assumptions the trivial solution of (2)-(3) is asymptotically stable, then the solution $z_i = \tilde{z}_i(t)$ of (1) is

asymptotically stable too.

Theorem: If only one root of the characteristic equation of the above defined linear system of approximation is greater than 1 with respect to its absolute value, then the periodic solution

Card 3/3 $z_i = \tilde{z}_i(t)$ of (1) is instable.

ASSOCIATION: Moscow Physical-Technical Institute (Moskovskiy fiziko-tehnicheskiy institut)

PRESENTED BY: I.G. Petrovskiy, Academician, April 23, 1957

SUBMITTED: April 18, 1957

AVAILABLE: Library of Congress